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Heats of Combustion of Some Tris (2,4-Pentanedionato) Metal (III) Complexes

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HEATS OF COMBUSTION OF SOME TRIS(2,4-PENTANEDIONATO)METAL(III) COMPLEXES

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ABSTRACT

The heats of combustion of tris(2,4-pentanedionato) metal(III) complexes of indium, lanthanum, neodymium, and samarium were measured in an oxygen bomb calorimeter and have been found to be -1875.8 ± 14.4 kcal/mole, -1837.6 ± 15.2 kcal/mole, -1891.8 ± 7.0 kcal/mole, and -1867.7 ± 6.6 kcal/mole; respectively. The energy of the metal-oxygen bond has been calculated using the appropriate thermochemical cycle and found to be 49.6 kcal/mole for indium, 80.8 kcal/mole for lanthanum, 67.9 kcal/mole for neodymium, and 67.1 kcal/mole for samarium.

Determinations of the heats of combustion of tris(2, 4-pentanedionato)iron(III) and tris(2,4-pentanedionato) aluminum were made to afford comparisons with values reported in the literature. Calculation of the energies of the metal-oxygen bonds shows the energy of the iron-oxygen bond to be 53.4 kcal/mole and the energy of the aluminum-oxygen bond to be 63.6 kcal/mole as compared to previously reported values of 59.4, 57.1 and 55.9 kcal/mole for the iron-oxygen bond; and 63.7 and 63 kcal/mole for the aluminum-oxygen bond.

HEATS OF COMBUSTION OF SOME TRIS(2,4-PENTANEDIONATO)METAL(III) COMPLEXES

INTRODUCTION

Various metal derivatives of 2,4-pentanedione have been studied recently to determine their heats of combustion and metal-oxygen bond energies (13,14,15,25). In a continuation of these studies, this paper reports the heats of combustion of the tris(2,4-pentanedionato) complexes of iron(III), aluminum, indium(III), lanthanum(III), neodymium(III), and samarium(III); of which the heats of combustion of the iron compound and the aluminum compound have been reported previously (13,14,15,25). The iron and aluminum compounds were chosen for the purpose of comparing the experimental values with literature values because the literature values were recent and because the pure compounds were available.

Using the suitable thermochemical cycle an approximation of the metal-oxygen bond energy can be made. The values for the thermochemical cycle are readily available from the literature with the exceptions of the heats of sublimation and the heats of combustion. By making estimates of the heats of sublimation and by using measured values for the heats of combustion, in the appropriate equations, the metal-oxygen bond energies have been determined.

2,4-pentanedione (acetylacetone) will be abbreviated as (AAH) and the tris(2,4-pentanedionato)metal(III) complexes will be abbreviated as $Fe(AA)_3$, $Al(AA)_3$, $In(AA)_3$, $La(AA)_3$, $Nd(AA)_3$, and $Sm(AA)_3$.

DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

I. APPARATUS

The heats of combustion were measured with a Parr series 1200 adiabatic oxygen bomb calorimeter equipped with a Parr 2602 automatic adiabatic control system. The temperatures before and after combustion were measured to the nearest 0.001 °C with a Leeds and Northrup 8160-B platinum resistance thermometer connected to a model 1551 Honeywell Mueller bridge. A Leeds and Northrup 9834 electronic d-c null detector was used in balancing the bridge. Identification of the metal oxide formed by the combustion was made using the X-ray powder diffraction technique, with a General Electric X-ray spectrophotometer.

II. EXPERIMENTAL PROCEDURE

A. Materials

Tris(2,4-pentanedionato)aluminum and tris(2,4-pentanedionato)iron(III) of minimum 99.0% purity were obtained from the J. T. Baker Chemical Company.

Tris(2,4-pentanedionato)metal(III) complexes of indium, lanthanum, neodymium, and samarium of minimum 95% purity were obtained from K & K Laboratories, Inc. These compounds were recrystalized from ethanol in two successive recrystal-

izations then kept, at room temperature, under a vacuum of 20μ for 48 hours to remove any traces of ethanol solvent prior to combustion. This extra precaution was taken with the compounds from K & K Laboratories because of the lower purity and because the $La(AA)_3$ as well as the resulting lanthanum oxide were blue. Lanthanum oxide has been reported as being white (24).

B. Calorimetric Measurements

The calorimeter was standarized at intervals using weighed samples of benzoic acid. The energy equivalent of the calorimeter was calculated to be 2444.27 cal/ °C.

The procedure has been described previously (15). Pellets of approximately 0.25 gram of the metal chelate were weighed to the nearest 0.0001 gram. The pellet was then placed in the center of a Parr 43AS metal combustion cup. Fifteen centimeters of standard Parr nickel-iron-chromium fuse wire No. 45C10 of 2.3 cal/cm was used with the Parr ignition transformer. The wire was formed into a small coil and suspended directly above the pellet with its lower part just touching the pellet. The oxygen bomb was then closed and charged with argon at a pressure of 6 psi above atmospheric pressure. The pressure was then raised to 20 atmospheres with oxygen. The extra length of fuse wire, combined with the reduced partial pressure of oxygen made careful positioning of the coil necessary. Sometimes the coil of fuse wire would glow hotly for a few

seconds before burning out rather than producing the flash usual at higher oxygen pressures. When no sample was present the fuse wire heated but did not burn, due to the low oxygen pressure. With a sample present, the increase in temperature due to combustion of the sample caused the fuse wire to burn out. The amount of resistance heat produced by the hotly glowing wire was determined by charging the bomb with the usual argon-oxygen gas mixture but no sample for combustion. Current was then passed through the wire. The time of current flow was noted and the temperature rise observed. The amount of resistance heat produced while the wire glowed was determined to be 7.6 cal/sec.

The operating procedure for the calorimeter follows that suggested in the Parr instruction manual. Two thousand grams of distilled water were placed in the calorimeter bucket. The pressurized bomb was then submerged in the water and electrical connections were made. The calorimeter was closed, the thermometers were lowered into the calorimeter, and the pump started. The temperature of the water jacket was brought into close agreement with the bucket temperature then the automatic cantroller was started. As soon as the cycling sequence became uniform, a timer was started. Four minutes later, the bucket temperature was determined, and the bomb was fired. Eight minutes after firing, the temperature of the bucket was again determined. Data for the temperature determinations are listed in

Appendix A. The calorimeter was opened and the bomb removed. The pressure in the bomb was slowly released then the bomb was opened and the contents analyzed.

Some of the samples burned poorly leaving large deposits of carbon on the walls of the bomb. The values for the heats of combustion of these samples are not reported here. A small amount of carbon was present in the metal cup after each combustion. The cup with the residual carbon was weighed to the nearest 0.1 milligram at room temperature. Then the cup and carbon were heated over a Meker burner for 5 to 10 minutes in order to remove the carbon. The cup was allowed to cool to room temperature and weighed to the nearest 0.1 milligram. The difference in weight was taken to be the weight of the carbon residue. For the carbon produced as an incomplete combustion product, thermal correction has been calculated using a value of 7.84 cal/mg for the heat of combustion of carbon (14).

Since combustion in the bomb takes place in an atmosphere of high oxygen content at high temperature and pressure, nitrogen in the bomb is oxidized and combines with water vapor to form nitric acid (HNO_3). These side reactions are important because they generate heat which can not be credited to the combustion of the sample and for which a correction must be made. All interior surfaces of the bomb were washed with a jet of distilled water and the washings were collected quantitatively in a beaker. Each sample was then titrated

with sodium hydroxide solution, with a thermal equivalent of 0.956 cal/ml, to determine the number of milliliters needed to neutralize the nitric acid. In computing the correction, it was assumed that all acid titrated was HNO_3 and that the heat of formation of a dilute nitric acid solution, under bomb conditions is 13.8 kg-cal per mole (20).

All values for the heats of combustion have been corrected for the heat produced by the fuse wire, for the unburned sample, and for the nitric acid produced. Data for these corrections are listed in Appendix B.

The combustion products, with the exception of the small amounts of carbon and nitric acid, are taken to be CO_2, H_2O, and the metal oxide. The oxides were mounted on microscope slides with a Duco cement-acetone mixture. Using the X-ray powder diffraction technique, the oxides have been identified as In_2O_3 (6-0416), La_2O_3 (5-0602), Nd_2O_3 (6-0408), and Sm_2O_3 (B form) (9-201). The data card numbers for the index to Powder Diffraction card file 1966 are given in parentheses. The oxides of iron and aluminum have been previously identified as αFe_2O_3 and αAl_2O_3 (15).

RESULTS AND DISCUSSION

The experimental data are listed in Table 1. Data for the temperature determination are given in Appendix A. Data for the thermal correction for unburned carbon, nitric acid produced, and resistance heat are listed in Appendix B. Data for ΔH determinations are given in Table 2. Results are given in Table 3.

ΔH_1 is the heat of sublimation of the metal. ΔH_{sub} is the heat of sublimation of the metal chelate. ΔH_c is the heat of combustion of the metal chelate. $\Delta H^\circ f_4$ is the heat of formation of the metal oxide in its standard state from the metal and oxygen in their standard state. $\Delta H^\circ f_1$ is the heat of formation of the keto form of 2,4-pentanedione in the liquid phase. ΔH_2 is the heat of vaporization of the keto form of 2,4-pentanedione. ΔH_{trans} is the heat of transition of 2,4-pentanedione from the keto form to the enol form. $\Delta H^\circ f_5$ is the heat of formation of carbon dioxide in its standard state from carbon and oxygen in their standard states. $\Delta H^\circ f_6$ is the heat of formation of water in its standard state from hydrogen and oxygen in their standard states. E(O-H) is the energy of the oxygen-hydrogen bond. E(H-H) is the energy of the hydrogen-hydrogen bond. E(O-O)

TABLE 1

EXPERIMENTAL DATA

SAMPLE	Total cal	Thermal correction cal	Net cal	sample weight gm	cal/gm
		$Fe(AA)_3$			
I	1398.12	26.5	1371.62	0.2571	5334.98
II	1476.34	15.5	1460.84	0.2745	5321.82
III	1082.81	23.0	1059.81	0.1992	5320.34
		$Al(AA)_3$			
I	1542.33	31.5	1510.83	0.2570	5878.73
II	1234.36	18.0	1216.36	0.2076	5859.13
III	1241.69	55.0	1186.69	0.2020	5874.70
IV	1740.32	66.0	1674.32	0.2852	5870.69
		$In(AA)_3$			
I	1244.13	24.0	1220.13	0.2684	4545.95
II	1060.81	6.5	1054.31	0.2310	4564.13
III	1662.10	18.0	1644.10	0.3622	4539.21
IV	1488.56	14.5	1474.06	0.3248	4538.36

TABLE 1 (Continued)

Sample	Total cal	Thermal correction cal	Net cal	sample weight gm	cal/gm
		$La(AA)_3$			
I	941.04	15.5	925.54	0.2210	4187.98
II	936.16	15.0	921.16	0.2199	4188.97
III	1014.37	6.0	1008.37	0.2375	4245.78
IV	701.51	18.5	683.01	0.1624	4205.70
V	760.17	14.0	746.17	0.1774	4206.13
VI	708.84	13.0	695.84	0.1651	4214.65
		$Nd(AA)_3$			
I	1107.25	24.0	1083.25	0.2529	4283.33
II	1048.59	-1.0	1049.59	0.2451	4282.30
III	1055.92	43.0	1012.92	0.2371	4272.14
IV	735.73	11.0	724.73	0.1692	4283.25
		$Sm(AA)_3$			
I	1126.81	44.0	1082.81	0.2599	4166.25
II	945.93	14.0	931.93	0.2234	4171.59
III	1129.25	22.5	1106.75	0.2653	4171.70
IV	1126.81	22.0	1104.81	0.2647	4173.81
V	1214.80	32.0	1182.80	0.2846	4156.02

TABLE 2

DATA FOR ΔH DETERMINATION

Sample	Molecular weight	$-\Delta E$ combustion kcal/mole	$-3RT$ kcal/mole	$-\Delta H$ kcal/mole
		$Fe(AA)_3$		
I	353.18	1884.21	1.78	1885.99
II	353.18	1879.56	1.78	1881.34
III	353.18	1879.04	1.78	1880.82
		$Al(AA)_3$		
I	324.31	1906.53	1.78	1908.31
II	324.31	1900.18	1.78	1901.96
III	324.31	1905.22	1.78	1907.00
IV	324.31	1903.92	1.78	1905.70
		$In(AA)_3$		
I	412.15	1873.61	1.78	1875.39
II	412.15	1881.10	1.78	1882.88
III	412.15	1870.84	1.78	1872.62
IV	412.15	1870.49	1.78	1872.27

TABLE 2 (Continued)

Sample	Molecular weight	$-\Delta E$ combustion kcal/mole	$-3RT$ kcal/mole	$-\Delta H$ kcal/mole
		$La(AA)_3$		
I	436.24	1826.97	1.78	1828.75
II	436.24	1827.40	1.78	1829.18
III	436.24	1852.18	1.78	1853.96
IV	436.24	1834.69	1.78	1836.47
V	436.24	1834.88	1.78	1836.66
VI	436.24	1838.60	1.78	1840.38
		$Nd(AA)_3$		
I	441.57	1891.39	1.78	1893.17
II	441.57	1890.94	1.78	1892.72
III	441.57	1886.45	1.78	1888.23
IV	441.57	1891.35	1.78	1893.13
		$Sm(AA)_3$		
I	447.68	1865.15	1.78	1866.93
II	447.68	1867.54	1.78	1869.32
III	447.68	1867.59	1.78	1869.37
IV	447.68	1868.53	1.78	1870.31
V	447.68	1860.57	1.78	1862.35

TABLE 3

RESULTS

$Fe(AA)_3$		
Average ΔE of combustion	-1880.94	kcal/mole
Average ΔH of combustion	-1882.72	kcal/mole
Standard deviation	±2.85	kcal/mole
Limits at 99% confidence	±16.31	kcal/mole
ΔH of combustion	-1882.7 ± 16.3	kcal/mole
$Al(AA)_3$		
Average ΔE of combustion	-1903.96	kcal/mole
Average ΔH of combustion	-1905.74	kcal/mole
Standard deviation	±2.74	kcal/mole
Limits at 99% confidence	± 8.00	kcal/mole
ΔH of combustion	-1905.7 ± 8.0	kcal/mole
$In(AA)_3$		
Average ΔE of combustion	-1874.01	kcal/mole
Average ΔH of combustion	-1875.79	kcal/mole
Standard deviation	± 4.93	kcal/mole
Limits at 99% confidence	±14.39	kcal/mole
ΔH of combustion	-1875.8 ± 14.4	kcal/mole

TABLE 3 (Continued)

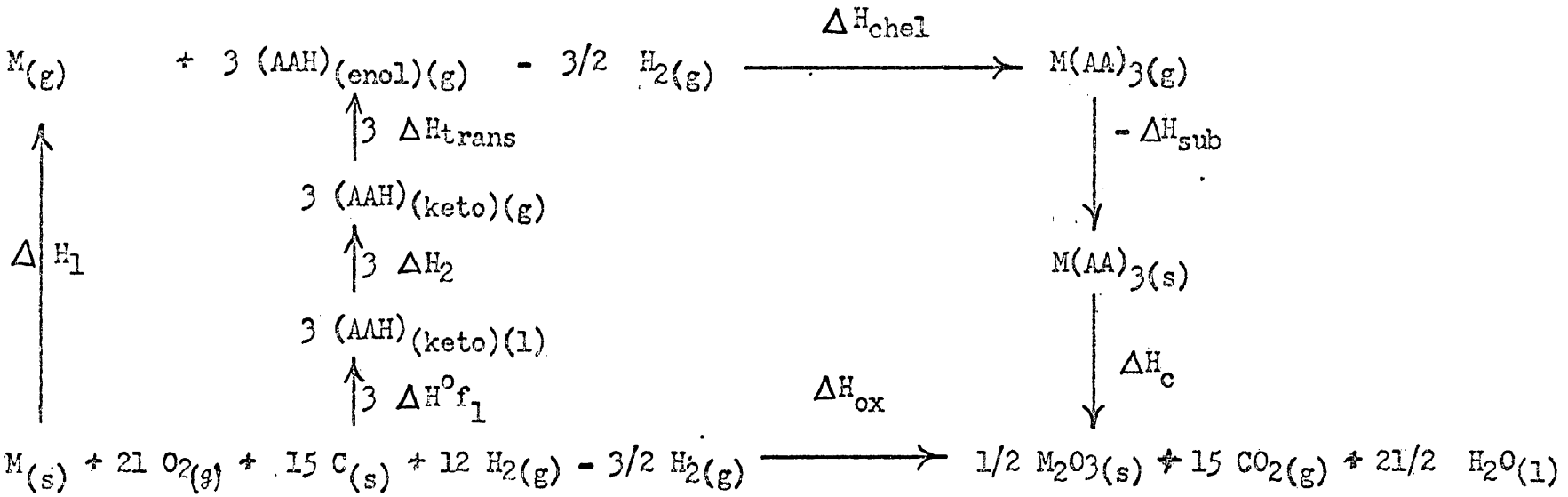
$La(AA)_3$		
Average ΔE of combustion	-1835.79	kcal/mole
Average ΔH of combustion	-1837.57	kcal/mole
Standard deviation	±9.24	kcal/mole
Limits at 99% confidence	±15.21	kcal/mole
ΔH of combustion	-1837.6 ±15.2	kcal/mole
$Nd(AA)_3$		
Average ΔE of combustion	-1890.03	kcal/mole
Average ΔH of combustion	-1891.81	kcal/mole
Standard deviation	±2.40	kcal/mole
Limits at 99% confidence	±7.00	kcal/mole
ΔH of combustion	-1891.8 ±7.0	kcal/mole
$Sm(AA)_3$		
Average ΔE of combustion	-1865.88	kcal/mole
Average ΔH of combustion	-1867.66	kcal/mole
Standard deviation	±3.22	kcal/mole
Limits at 99% confidence	±6.63	kcal/mole
ΔH of combustion	-1867.7 ±6.6	kcal/mole

is the energy of the oxygen-oxygen bond. ΔH_{ox} is the heat of oxidation of the metal going to M_2O_3, carbon to CO_2, and H_2 to H_2O. $\Delta H^{\circ}f_2$ is the heat of formation of the metal chelate in its standard state from the elements in their standard states. ΔH_{chel} is the heat of formation of the metal chelate in the gaseous state from $M_{(g)}$ and $(AAH)_{(g)}$. E(M-O), the energy of the metal-oxygen bond, is calculated from the thermochemical cycle illustrated in Figure 1 (13) assuming the six metal-oxygen bonds to be of equal strength. ΔHf_3, the heat of formation of the solid metal oxide from the metal and oxygem in the gaseous state, is calculated from the thermochemical cycle illustrated in Figure 2. The values of these quantities are listed in tables 4 and 5.

With the experimental values for the heats of combustion of the metal chelate available, all the values needed to calculate the metal-oxygen bond energies are known except some of the heats of sublimation. The value for the ΔH_{sub} of $Ga(AA)_3$ has been used as an estimate for the heats of sublimation of $In(AA)_3$, $La(AA)_3$, $Nd(AA)_3$, and $Sm(AA)_3$. There is some justification for using this value as an estimate. Assuming the range of the liquid phase of the metal chelates is comparable to the reported ranges for $Cr(AA)_3$, $Th(AA)_3$, and $Al(AA)_3$ (24); then the boiling points may be estimated. Using Trouton's rule and assuming the heat of fusion to be approximately 20% the heat of vaporization, the heats of sublimation were calculated. The values

FIGURE 1

THERMOCHEMICAL CYCLE



$\Delta H_{chel} = \Delta H_{ox} - \Delta H_1 - 3\Delta H^\circ f_1 - 3\Delta H_2 - 3\Delta H_{trans} + \Delta H_{sub} - \Delta H_c$

$\Delta H_{chel} = 3\,E(O\text{-}H) - 6\,E(M\text{-}O) - 3/2\,E(H\text{-}H) - 3/2\,RT$

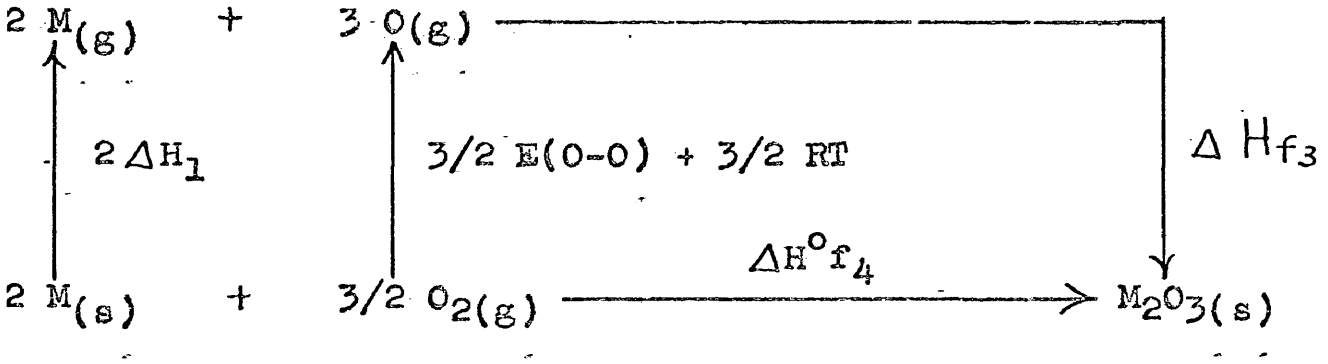
$\Delta H^\circ f_2 = \Delta H_{ox} - \Delta H_c$

$\Delta H_{ox} = 1/2\,\Delta H^\circ f_4 + 15\,\Delta H^\circ f_5 + 21/2\,\Delta H^\circ f_6$

FIGURE 2

HEAT OF FORMATION OF THE SOLID METAL OXIDE

FROM THE METAL AND OXYGEN IN THE GASEOUS STATE



$\Delta Hf_3 = \Delta H^{\circ}f_4 - 2\Delta H_1 - 3/2\ E(O-O) - 3/2\ RT$

TABLE 4

DATA FOR THERMOCHEMICAL CYCLE

Compound	ΔH_1 kcal/mole	ΔH_{sub} kcal/mole	ΔH_c kcal/mole	$\Delta H^\circ f_4$ kcal/mole
$Fe(AA)_3$	99.83(25)	27.93(22)	-1882.7(**)	-191.7(23)
$Al(AA)_3$	77.4 (1)	25.99(22)	-1905.7(**)	-400.29(6)
$Ga(AA)_3$	65.00(16)	30.60(18)	-1896.8(15)	-261.05(17)
$In(AA)_3$	57.51(16)	30.6 (*)	-1875.8(**)	-221.27(7)
$Sc(AA)_3$	90.98(5)	30.6 (*)	-1907.3(25)	-456.16(8)
$La(AA)_3$	102.96 (5)	30.6 (*)	-1837.6(**)	-428.6(3)(11)
$Nd(AA)_3$	78.33(5)	30.6 (*)	-1891.8(**)	-432.15(10)
$Sm(AA)_3$	48.59(5)	30.6 (*)	-1867.7(**)	-433.89(12)

* estimated value
** this paper

TABLE 4 (Continued)

$\Delta H^{o}f_1$	-100.95	kcal/mole	(25)
ΔH_2	16.5	kcal/mole	(25)
ΔH_{trans}	-3.9	kcal/mole	(4)
$\Delta H^{o}f_5$	-94.05	kcal/mole	(2)
$\Delta H^{o}f_6$	-68.32	kcal/mole	(2)
E(O-H)	109.4	kcal/mole	(21)
E(H-H)	103.2	kcal/mole	(21)
E(O-O)	117.2	kcal/mole	(21)

TABLE 5

CALCULATIONS FROM THERMOCHEMICAL CYCLE

	ΔH_{ox} kcal/ mole	$\Delta H^{o}f_{2}$ kcal/ mole	ΔH_{chel} kcal/ mole	ΔHf_{3} kcal/ mole	E(M-O) kcal/ mole
$Fe(AA)_3$	-2223.96	-341.26	-148.11	-568.05	53.4
$Al(AA)_3$	-2328.26	-422.56	-208.92	-731.78	63.6
$Ga(AA)_3$	-2258.64	-361.84	-131.19	-567.74	50.6
$In(AA)_3$	-2238.75	-362.95	-124.81	-512.98	49.6
$Sc(AA)_3$	-2356.19	-448.89	-244.22	-814.81	69.5
$La(AA)_3$	-2342.41	-504.81	-312.12	-811.21	80.8
$Nd(AA)_3$	-2344.19	-452.39	-235.07	-765.50	67.9
$Sm(AA)_3$	-2345.06	-477.36	-230.30	-707.76	67.1

for $\triangle H_{sub}$ estimated this way were found to be within a range of approximately 2 kcal/mole of each other and approximately one half the experimentaly determined value of 30.6 kcal/mole for $Ga(AA)_3$ (18). Since 2 kcal/mole change in the heat of sublimation only changes the bond energy by one third kcal/mole and since the $Ga(AA)_3$ value was experimentaly determined, the value of 30.6 kcal/mole was used as an estimate in the bond energy calculations.

The energy of the iron-oxygen bond has been calculated to be 53.4 kcal/mole as compared to values of 57.1 (15), 59.4 (13), and 55.9 (25) kcal/mole previously reported.

The aluminum-oxygen bond energy of 63.6 kcal/mole was found to be in close agreement with the previously reported values of 63 (14) and 63.7 (15) kcal/mole.

In order that the bond energies of all compounds would be determined from consistent values and the same thermochemical cycle, the values for the gallium-oxygen bond of 50.6 kcal/mole and the scandium-oxygen bond of 69.5 kcal/mole were calculated. The previously reported value for the gallium-oxygen bond is 51.1 kcal/mole (15) and for the scandium-oxygen bond is 66.6 kcal/mole (25).

An estimate of the error in the bond energy calculation has been made. The results of this estimate are given in Table 6. In order to make the estimate, the error in measurement was determined for the values in the thermochemical cycle which differ among the compounds used. The

bond energy calculation was then made to determine a minimum and a maxium value. The errors in the calculation of E(M-O) range from ± 0.9 kcal/mole for E(Sc-O) to ± 3.4 kcal/mole for E(Fe-O). The estimates made in this way are not estimates of absolute error since the values in the thermochemical cycle which do not change among the metal(III) complexes were not included. The estimates are only useful in comparing the E(M-O) among the compounds studied.

A graph of log E(M-O) vs. log $(R_i + R_o)$ was constructed. R_i is the radius of the tervalent metal ion in Angstrom units. R_o is the radius of the oxygen ion in Angstrom units. E(M-O) is in kcal/mole. A straight line can be constructed through the Ga, Fe, and In values with the same slope as a line through the Sm, Nd, and Sc values. The large value for E(Al-O) possibly is due to the small ionic size of the aluminum which would be expected to have a greater polarization effect on the oxygen. The value for E(La-O) is somewhat greater than expected. The graph is illustrated in Figure 3.

The bond energies in increasing order give the series In, Ga, Fe, Al, Sm, Nd, Sc, La. In the series In, Ga, Al, the much higher value for the bond energy of the aluminum-oxygen bond seems to be due to the higher value for the heat of formation of the aluminum oxide.

The neodymiun and samarium bond energies are rather close as would be expected because of their great similarity. However, the energy of the lanthanum-oxygen bond is higher

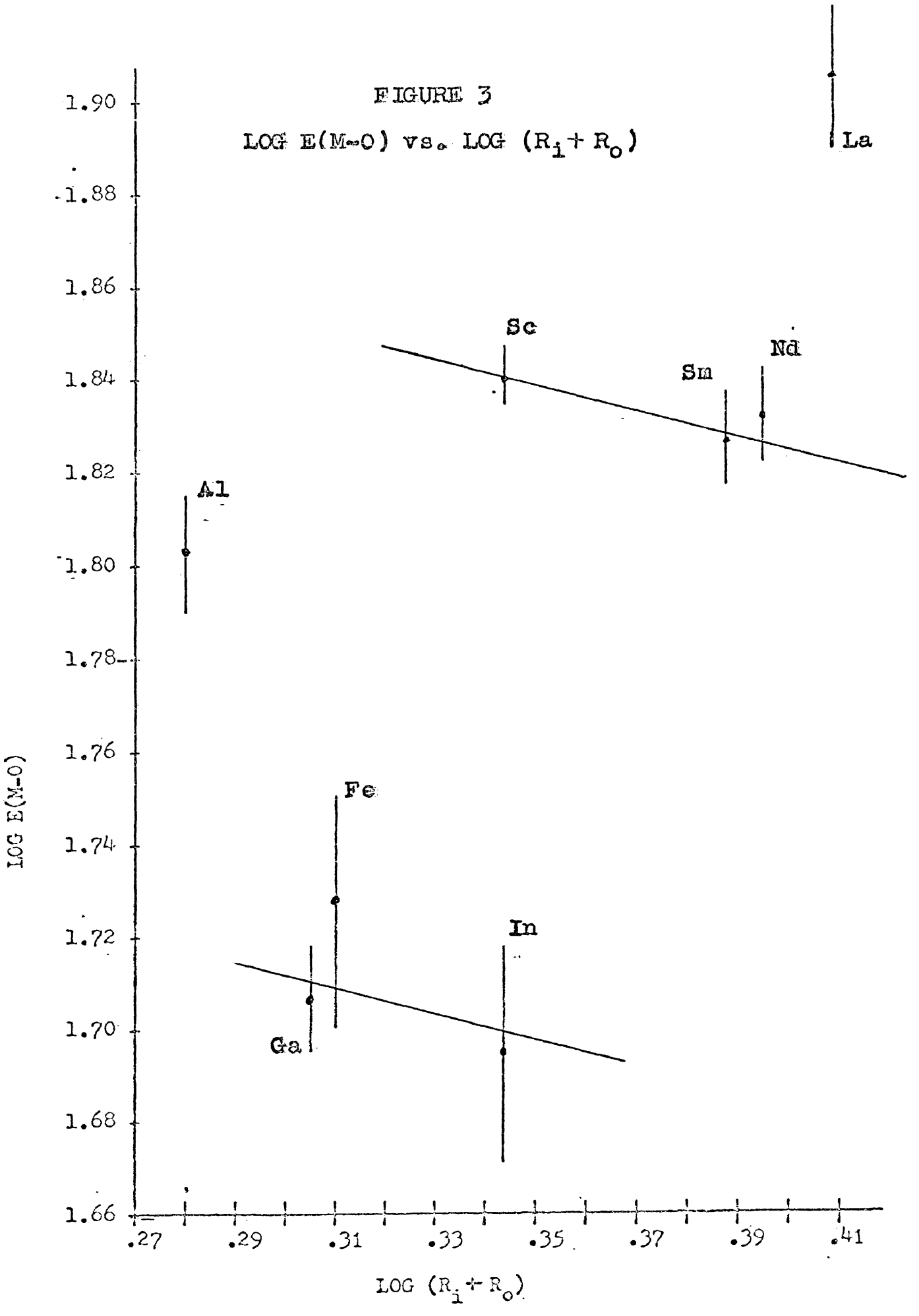
TABLE 6

ESTIMATE OF ERROR IN BOND ENERGY CALCULATIONS

	E(M-O) kcal/mole	
	low value	high value
Fe-O	50.1	56.8
Al-O	61.8	65.3
Ga-O	49.0	52.2
In-O	46.7	52.4
Sc-O	68.6	70.3
La-O	78.0	83.5
Nd-O	66.5	69.3
Sm-O	65.7	68.5

FIGURE 3

LOG E(M-O) vs. LOG $(R_i + R_o)$



than might be expected. The Sm, Nd, La, values seem to progress smoothly in Tables 4 and 5 with the exception of ΔH_c for $La(AA)_3$ and the values calculated from this quantity. As was mentioned earlier the $La(AA)_3$ and the resulting oxide were both blue. The trivalent lanthanum ion is colorless (19) and the La_2O_3 is reported to be white (24).

Since a change in weight of 1% could make a difference of 1% in the value of ΔH_c, the $La(AA)_3$, $Nd(AA)_3$, $Sm(AA)_3$, and $In(AA)_3$ were recrystalized from ethanol in an attempt to remove any impurity that might be present. The recrystalized compounds were found to produce higher values for ΔH_c. The values reported are for recrystalized compounds. The blue color in the lanthanum compound and the resulting blue oxide were still observed after recrystalization. In order to determine if the blue color were due to some oxygen deficient form of lanthanum oxide, the oxide was placed in a platinum crucible and heated in an oven at 1050°C for over one hour. The material before and after heating in the oven appeared to be the same. X-ray slides were made of both materials. The X-ray diffraction patterns for both materials were identical and corresponded to the card index (5-0602) for La_2O_3.

A limitation on the accuracy of the method is the determination of temperature. The temperatures were read to the nearest 0.001 °C consequently the value for the temperature difference could have varied by 0.002 °C. A change in

the value of Δt of 0.002 °C could change the value of ΔH_c by as much as 10 kcal/mole. The limits at 99% confidence were calculated using Student's t formula (26). Although the precision of measurement is not as good as that obtained from the combustion of some other organic compounds, it is good enough to afford a comparsion among the compounds studied.

APPENDIX A

DATA FOR TEMPERATURE DETERMINATIONS

Sample	Resistance Readings (ohms) Normal	Reverse	Temperature °C	Δt
		$Fe(AA)_3$		
I	28.1220	28.1229	24.864	
	28.1799	28.1807	25.436	0.572
II	28.1176	28.1185	24.821	
	28.1788	28.1797	25.425	0.604
III	28.1439	28.1448	25.081	
	28.1888	28.1897	25.524	0.443
		$Al(AA)_3$		
I	27.8124	27.8133	21.808	
	27.8764	27.8772	22.439	0.631
II	28.2733	28.2742	26.359	
	28.3244	28.3253	26.864	0.505
III	28.2161	28.2170	25.794	
	28.2675	28.2684	26.302	0.508
IV	28.0900	28.0909	24.548	
	28.1620	28.1630	25.260	0.712

APPENDIX A (Continued)

Sample	Resistance Readings (ohms) Normal	Reverse	Temperature °C	At
		$In(AA)_3$		
I	28.2437	28.2446	26.067	
	28.2952	28.2961	26.576	0.509
II	28.2632	28.2641	26.259	
	28.3071	28.3080	26.693	0.434
III	28.1798	28.1807	25.435	
	28.2486	28.2495	26.115	0.680
IV	28.2023	28.2032	25.658	
	28.2640	28.2649	26.267	0.609
		$La(AA)_3$		
I	28.1646	28.1655	25.285	
	28.2036	28.2044	25.670	0.385
II	28.1685	28.1694	25.324	
	28.2073	28.2082	25.707	0.383
III	28.3122	28.3131	26.743	
	28.3541	28.3550	27.158	0.415
IV	27.9333	27.9342	23.001	
	27.9624	27.9633	23.288	0.287
V	27.9670	27.9679	23. 334	
	27.9985	27.9994	23.645	0.311
VI	28.2023	28.2032	25.658	
	28.2316	28.2326	25.948	0.290

APPENDIX A (Continued)

Sample	Resistance Readings (ohms) Normal	Reverse	Temperature °C	Δt
		$Nd(AA)_3$		
I	28.2370	28.2379	26.000	
	28.2828	28.2837	26.453	0.453
II	28.2581	28.2590	26.209	
	28.3015	28.3024	26.638	0.429
III	27.9181	27.9190	22.851	
	27.9619	27.9628	23.283	0.432
IV	28.3903	28.3919	27.515	
	28.4206	28.4216	27.815	0.300
		$Sm(AA)_3$		
I	28.2451	28.2460	26.080	
	28.2917	28.2926	26.541	0.461
II	27.9362	27.9371	23.030	
	27.9754	27.9763	23.417	0.387
III	28.1341	28.1349	24.983	
	28.1808	28.1817	25.445	0.462
IV	28.1646	28.1655	25.285	
	28.2123	28.2132	25.746	0.461
V	28.1986	28.1995	25.621	
	28.2489	28.2498	26.118	0.497

APPENDIX B

DATA FOR THERMAL CORRECTION

Sample	wire corr. cal	resist. heat cal	HNO_3 corr. cal	carbon corr. cal	Total corr. cal
		$Fe(AA)_3$			
I	25.5	0	5	4	26.5
II	12.5	0	7	4	15.5
III	24.0	0	3	4	23.0
		$Al(AA)_3$			
I	19.5	14	3	5	31.5
II	19.0	0	4	5	18.0
III	33.0	23	4	5	55.0
IV	14.0	42	15	5	66.0
		$In(AA)_3$			
I	29.0	0	4	9	24.0
II	17.5	0	2	13	6.5
III	27.0	0	2	11	18.0
IV	21.5	0	4	11	14.5

APPENDIX B (Continued)

Sample	wire corr. cal	resist. heat cal	HNO_3 corr. cal	carbon corr. cal	Total corr. cal
			$La(AA)_3$		
I	21.5	0	5	11	15.5
II	17.0	0	3	5	15.0
III	15.0	0	2	11	6.0
IV	25.5	0	4	11	18.5
V	22.0	0	5	13	14.0
VI	21.0	0	3	11	13.0
			$Nd(AA)_3$		
I	30.0	0	3	9	24.0
II	15.0	0	2	18	-1.0
III	30.0	30	4	21	43.0
IV	18.0	0	2	9	11.0
			$Sm(AA)_3$		
I	31.0	30	4	21	44.0
II	21.0	0	4	11	14.0
III	27.5	0	4	9	22.5
IV	27.0	0	4	9	22.0
V	34.0	0	7	9	32.0

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